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**PATENT APPLICATION**  
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**APPLICATION FOR  
UNITED STATES LETTERS PATENT**

**TO ALL WHOM IT MAY CONCERN:**

**Be it known that WE, Hany Aziz, Nan-Xing Hu, Zoran D. Popovic, and James M. Duff, have invented**

**OLEDs HAVING LIGHT ABSORBING ELECTRODE**

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**BACKGROUND OF THE INVENTION**

Organic light emitting devices (OLEDs) represent a promising technology for display applications. A typical organic light emitting device includes a transparent first electrode, which usually acts as a hole-injecting anode; a luminescent region comprising one or more electroluminescent organic layer(s); and a second electrode (also called a "back electrode"), which usually acts as an electron-injecting cathode. In order to facilitate electron injection from the back electrode into the electroluminescent layer(s), the back electrode generally is formed of a low work function metal, and therefore is highly reflective. When a voltage is applied across the first and second electrodes, light is emitted from the electroluminescent layer(s) and through the transparent anode. When viewed under high ambient illumination, the reflective back electrode reflects a substantial amount of the ambient illumination to the observer, which results in higher ratios of reflected illumination as compared to the device's own emission, which results in "washout" of the displayed image.

In order to improve the contrast of electroluminescent displays in general, light absorbing layers as described, for example, in U.S. Patent 4,287,449, or optical interference members as described, for example, in U.S. Patent 5,049,780, have been used to reduce the ambient illumination reflection. Both of these approaches involve the use of optical films made of materials that are generally non-conductive. These properties limit the applicability of such materials to organic light emitting devices, which, unlike inorganic electroluminescent phosphor devices, require the direct injection of charges from the electrodes to the electroluminescent layer(s). In addition, the fabrication of such optical films, essentially from dielectric inorganic materials, often requires the use of sputtering or electron beam evaporation techniques. These fabrication techniques require additional instrumentation to be incorporated into the otherwise relatively simple fabrication process of organic light emitting devices by thermal evaporation or spin coating techniques. Also, in cases using optical interference effects for achieving improved contrast, such as disclosed, for example, in U.S. Patent 5,049,780, it is usually required to use more than one optical film in order to achieve the desired improvement, which is disadvantageous to the fabrication

1 process. Furthermore, the resulting improvement in display contrast is inevitably  
2 dependent on the viewing angle.

3 Thus, there is a need, addressed by the present invention, for new OLEDs that  
4 avoid or minimize a number of the disadvantages described above for conventional  
5 electroluminescent devices.

6 Organic light emitting devices are disclosed in the following:

7 Pending US Serial No. 09/800,716 (titled "cathodes for electroluminescent  
8 devices having improved contrast and reduced dark spot growth"), assigned to Xerox  
9 Corporation; and

10 O. Renault et al., "A low reflectivity multilayer cathode for organic light-  
11 emitting diodes," *Thin Solid Films*, Vol. 379, pp. 195-198 (December 8, 2000);

12 International Application Publication No. WO 01/08240 A1; and

13 David Johnson et al., "Contrast Enhancement of OLED Displays,"  
14 [http://www.luxell.com/pdfs/OLED\\_tech\\_ppr.pdf](http://www.luxell.com/pdfs/OLED_tech_ppr.pdf), pp. 1-3 (April 2001).

## 15 **SUMMARY OF THE INVENTION**

16  
17  
18 The present invention is accomplished in embodiments by providing an organic  
19 light emitting device comprising:

20 a first electrode;

21 a second electrode; and

22 a luminescent region including an organic electroluminescent material between  
23 the first electrode and the second electrode, wherein one of the first electrode and the  
24 second electrode includes both a substantially transparent charge injecting layer  
25 adjacent to the luminescent region and an electrically conductive light absorbing layer.

26 There is also provided in embodiments an organic light emitting device  
27 comprising in sequence:

28 (a) a cathode including:

29 (i) an electrically conductive light absorbing layer, and

30 (ii) a substantially transparent electron injecting layer;

31 (b) a luminescent region including an organic electroluminescent material; and

32 (c) an anode that is substantially transparent to light.

33 There is provided in additional embodiments an organic light emitting device  
34 comprising in sequence:

35 (a) a cathode that is substantially transparent to light;

36 (b) a luminescent region including an organic electroluminescent material; and

- 1 (c) an anode including:  
2 (i) a substantially transparent hole injecting layer, and  
3 (ii) an electrically conductive light absorbing layer.  
4

## 5 **BRIEF DESCRIPTION OF THE DRAWINGS**

6  
7 Other aspects of the present invention will become apparent as the following  
8 description proceeds and upon reference to the Figures which represent illustrative  
9 embodiments:

10 FIG. 1 is a schematic, elevational view in cross-section of a first embodiment of  
11 the present OLED;

12 FIG. 2 is a schematic, elevational view in cross-section of a second embodiment  
13 of the present OLED;

14 FIG. 3 is a schematic, elevational view in cross-section of a third embodiment of  
15 the present OLED; and

16 FIG. 4 is a schematic, elevational view in cross-section of a fourth embodiment  
17 of the present OLED.

18 Unless otherwise noted, the same reference numeral in different Figures refers to  
19 the same or similar feature.  
20

## 21 **DETAILED DESCRIPTION**

22  
23 The present organic light emitting device is composed of at least a first  
24 electrode; a second electrode; and a luminescent region including an organic  
25 electroluminescent material between the first electrode and the second electrode,  
26 wherein one of the first electrode and the second electrode includes both a substantially  
27 transparent charge injecting layer adjacent to the luminescent region and an electrically  
28 conductive light absorbing layer. Either the cathode or the anode can include the  
29 charge injecting layer and the electrically conductive light absorbing layer. The charge  
30 injecting layer may be either an electron injecting layer (in the case of a cathode) or a  
31 hole injecting layer (in the case of an anode). The present organic light emitting device  
32 may include a substrate either as a separate layer adjacent to one of the electrodes or  
33 incorporated into one of the electrodes (e.g., the electrically conductive light absorbing  
34 layer that is part of an electrode includes in embodiments a substrate material to result  
35 in an electrically conductive light absorbing substrate).

1 A first exemplary embodiment is seen in FIG. 1 where the organic light emitting  
2 device 2A is composed of in the depicted sequence: a substrate 4A; an anode 6A; a  
3 luminescent region 8A; and a cathode 10A including a substantially transparent  
4 electron injecting layer 12A, an optional buffer layer 14A, an electrically conductive  
5 light absorbing layer 16A, and an optional metallic layer 18A. In FIG. 1, the anode 6A  
6 and substrate 4A are substantially transparent so that light emitted within the  
7 luminescent region can reach the viewer.

8 As used herein, the phrase "substantially transparent" indicates a significant level  
9 of light transmissivity through a layer such as for example at least about 50%  
10 transmissivity, particularly at least about 70% transmissivity.

11 A second exemplary embodiment is seen in FIG. 2 where the organic light  
12 emitting device 2B is composed of in the depicted sequence: an anode 6B; a  
13 luminescent region 8B; and a cathode 10B including a substantially transparent electron  
14 injecting layer 12B, an optional buffer layer 14B, an electrically conductive light  
15 absorbing layer 16B, and an optional metallic layer 18B; and a substrate 4B. In FIG. 2,  
16 the anode 6B is substantially transparent so that light emitted within the luminescent  
17 region can reach the viewer.

18 A third exemplary embodiment is seen in FIG. 3 where the organic light emitting  
19 device 2C is composed of in the depicted sequence: a substrate 4C; a cathode 10C; a  
20 luminescent region 8C; and an anode 6C including a substantially transparent hole  
21 injecting layer 12C, an optional buffer layer 14C, an electrically conductive light  
22 absorbing layer 16C, and an optional metallic layer 18C. In FIG. 3, the cathode 10C  
23 and substrate 4C are substantially transparent so that light emitted within the  
24 luminescent region can reach the viewer.

25 A fourth exemplary embodiment is seen in FIG. 4 where the organic light  
26 emitting device 2D is composed of in the depicted sequence: a cathode 10D; a  
27 luminescent region 8D; and an anode 6D including a substantially transparent hole  
28 injecting layer 12D, an optional buffer layer 14D, an electrically conductive light  
29 absorbing layer 16D, and an optional metallic layer 18D; and a substrate 4D. In FIG. 4,  
30 the cathode 10D is substantially transparent so that light emitted within the luminescent  
31 region can reach the viewer.

32 FIGS. 1-4 depict a single light absorbing layer. In other embodiments, however,  
33 two or more light absorbing layers may be present.

34 The reason for improved contrast by the present invention is now discussed. The  
35 incorporation of a substantially transparent charge injecting layer (12A, 12B, 12C,

1 12D) results in the transmission of a substantial portion of ambient light reaching this  
2 layer, and therefore, the portion of ambient light that is reflected back from this layer to  
3 the viewer is substantially reduced. Furthermore, the incorporation of an electrically  
4 conductive light absorbing layer (16A, 16B, 16C, 16D) absorbs a substantial portion of  
5 the ambient light that is transmitted through the charge injecting layer (and the optional  
6 buffer layer), and therefore, a substantial portion of the ambient light that reaches the  
7 optional metallic layer is not reflected back to the viewer, and hence image washout is  
8 substantially reduced.

9 The amount of light absorption of the light absorbing layer depends on the  
10 extinction coefficient of the light absorbing material comprising the light absorbing  
11 layer, as well as on the thickness of the light absorbing layer, where, in general, a  
12 higher value for the extinction coefficient and a larger layer thickness lead to more light  
13 absorption, and hence are more desirable in embodiments. Also, the higher the  
14 extinction coefficient of the material, the less the thickness needed to achieve a certain  
15 amount of light absorption.

16 The multi-layer electrode of the present OLED (having the charge injecting  
17 layer and the electrically conductive light absorbing layer) exhibits as a whole both  
18 lateral electrical conductivity (across the width of the electrode) and cross directional  
19 electrical conductivity (through the thickness of the electrode). However, in certain  
20 embodiments, a layer of the multi-layer electrode such as the optional buffer layer, may  
21 exhibit cross directional conductivity but not lateral conductivity. That each of the  
22 electrode layers is considered part of the electrode arises from the fact that each of (1)  
23 the charge injecting layer, (2) the electrically conductive light absorbing layer, and the  
24 (3) the optional protective metallic layer contribute to both lateral conduction and cross  
25 directional conduction. The optional buffer layer, being made of an insulative material,  
26 does not contribute to lateral conduction, but is considered part of the electrode because  
27 if the buffer layer is thin enough, it can sustain cross directional conduction. In  
28 embodiments of the present invention, the multi-layer electrode is a stack of adjacent  
29 layers where each layer exhibits a cross directional electrical conductivity with an  
30 ohmic resistance less than about 100 ohms, particularly less than about 10 ohms, and  
31 especially less than about 1 ohm.

32 A substantially transparent substrate can comprise various suitable materials  
33 including, for example, polymeric components, glass, quartz and the like. Suitable  
34 polymeric components include, but are not limited to polyesters such as MYLAR®,  
35 polycarbonates, polyacrylates, polymethacrylates, polysulfones, and the like. Other

1 substrate materials can also be selected provided, for example, that the materials can  
2 effectively support the other layers, and do not interfere with the device functional  
3 performance.

4 An opaque substrate can comprise various suitable materials including, for  
5 example, polymeric components like polyesters such as MYLAR<sup>®</sup>, polycarbonates,  
6 polyacrylates, polymethacrylates, polysulfones, and the like, which contain coloring  
7 agents or dyes such as carbon black. The substrate can also be comprised of  
8 silicon such as amorphous silicon, polycrystalline silicon, single crystal silicon, and the  
9 like. Another class of materials that can be used in the substrate are ceramics such as  
10 metallic compounds like metal oxides, halides, hydroxides, sulfides and others.

11 The substrate may have a thickness ranging for example from about 10 to about  
12 5,000 micrometers, and more particularly from about 25 to about 1,000 micrometers.

13 A substantially transparent anode (such as that used in the OLED devices of  
14 FIGS. 1-2) can comprise suitable positive charge injecting materials such as indium tin  
15 oxide (ITO), silicon, tin oxide, and metals with a work function ranging from about 4  
16 eV to about 6 eV such as gold, platinum, and palladium. Other suitable materials for  
17 the anode include, but are not limited to, electrically conductive carbon,  $\pi$ -conjugated  
18 polymers such as polyaniline, polythiophene, polypyrrole, and the like having, for  
19 example, a work function equal to, or greater than, about 4 eV, and particularly from  
20 about 4 eV to about 6 eV. A substantially transparent anode can comprise very thin  
21 substantially transparent metallic layers, comprising a metal with a work function  
22 ranging from about 4 eV to about 6 eV such as gold, palladium and the like, having a  
23 thickness, for example, from about 10 Å to about 200 Å, and, particularly, from about  
24 30 Å to about 100 Å. Additional suitable forms of the anode are disclosed in U.S.  
25 Patents 4,885,211 and 5,703,436, which are incorporated herein by reference in their  
26 entirety.

27 The thickness of the substantially transparent anode can range from about 10 Å to  
28 about 50,000 Å, with the preferred range depending on the optical constants of the  
29 anode material. One illustrative range of anode thickness is from about 300 Å to about  
30 3,000 Å. Of course, a thickness outside of this range can also be used.

31 A substantially transparent cathode (such as that used in the OLED devices of  
32 FIGS. 3-4) can comprise very thin substantially transparent metallic layers comprising  
33 a metal with a work function ranging from about 2 eV to about 4 eV, such as Mg, Ag,  
34 Al, Ca, In, Li and their alloys such as Mg:Ag alloys, comprised of, for example, from  
35 about 80 to 95 volume percent of Mg and about 20 to about 5 volume percent of Ag,

1 and Li:Al alloys, comprised of, for example, from about 90 to 99 volume percent of Al,  
2 and from about 10 to about 1 volume percent of Li, and the like, having a thickness,  
3 for example, from about 10 Å to about 200 Å, and, particularly, from about 30 Å to  
4 about 100 Å. Other substantially transparent cathodes are disclosed in US Serial No.  
5 09/800,716, cited earlier, and incorporated herein by reference in its entirety, such as  
6 cathodes comprising a layer, of thickness from about 100 Å to about 10,000 Å, and  
7 particularly from about 500 Å to about 5,000 Å, comprised of a metal, an organic  
8 material, and a third component which can be a metal, an organic material, or any other  
9 material. One embodiment is a cathode composed of a layer comprised of about 47.4  
10 volume percent of Mg, about 5.2 volume percent of Ag, and about 47.4 volume percent  
11 of tris(8-hydroxyquinoline) aluminum (AlQ<sub>3</sub>). Additional suitable forms of  
12 substantially transparent cathodes are disclosed in U.S. Patent 5,703,436, which is  
13 incorporated herein by reference in its entirety.

14 The thickness of the substantially transparent cathode can range from about 10 Å  
15 to about 50,000 Å, with the preferred range depending on the optical constants of the  
16 cathode material. One illustrative range of cathode thickness is from about 30 Å to  
17 about 100 Å. Another illustrative range is from about 50 Å to about 500 Å. Of course,  
18 a thickness outside of this range can also be used.

19 A substantially transparent electron injecting layer can include very thin  
20 substantially transparent metallic layers, composed of a metal with a work function  
21 ranging from about 2 eV to about 4 eV, such as Mg, Ag, Al, Ca, In, Li and their alloys  
22 such as Mg:Ag alloys composed of, for example, from about 80 to 95 volume percent  
23 of Mg and about 20 to about 5 volume percent of Ag, and Li:Al alloys, composed of,  
24 for example, from about 90 to 99 volume percent of Al, and from about 10 to about 1  
25 volume percent of Li, and the like, having a thickness, for example, from about 10 Å to  
26 about 200 Å, and, particularly, from about 30 Å to about 100 Å. Other substantially  
27 transparent electron injecting layers are disclosed in US Serial No. 09/800,716, cited  
28 earlier, and incorporated herein by reference in its entirety, such as a layer, of  
29 thickness from about 100 Å to about 10,000 Å, and particularly from about 500 Å to  
30 about 5,000 Å, comprised of a metal, an organic material, and a third component which  
31 can be a metal, an organic material, or any other material. One embodiment is a layer  
32 composed of about 47.4 volume percent of Mg, about 5.2 volume percent of Ag, and  
33 about 47.4 volume percent of tris(8-hydroxyquinoline) aluminum (AlQ<sub>3</sub>).

34 The thickness of a substantially transparent electron injecting layer can range  
35 from about 10 Å to about 50,000 Å, with the preferred range depending on the optical



1 constants of the cathode material. One illustrative range of thickness of the electron  
2 injecting layer is from about 30 Å to about 100 Å. Another illustrative range is from  
3 about 50 Å to about 500 Å. Of course, a thickness outside of this range can also be  
4 used.

5 A substantially transparent hole injecting layer can be composed of suitable  
6 positive charge injecting materials such as indium tin oxide (ITO), silicon, tin oxide,  
7 and metals with a work function ranging from about 4 eV to about 6 eV, such as, gold,  
8 platinum, and palladium. Other suitable materials for the hole injecting layer include,  
9 but are not limited to, electrically conductive carbon,  $\pi$ -conjugated polymers such as  
10 polyaniline, polythiophene, polypyrrole, and the like having, for example, a work  
11 function equal to, or greater than, about 4 eV, and particularly from about 4 eV to about  
12 6 eV. A substantially transparent hole injecting material can be composed of very thin  
13 substantially transparent metallic layers, comprising a metal with a work function  
14 ranging from about 4 eV to about 6 eV, such as gold, palladium and the like, having a  
15 thickness, for example, from about 10 Å to about 200 Å, and, particularly, from about  
16 30 Å to about 100 Å. Additional suitable forms of hole injecting layers are disclosed in  
17 U.S. Patents 4,885,211 and 5,703,436, which are incorporated herein by reference in  
18 their entirety.

19 The thickness of a substantially transparent hole injecting layer can range, for  
20 example, from about 10 Å to about 50,000 Å, with the preferred range depending on  
21 the optical constants of the selected material. One illustrative range of thickness of the  
22 hole injecting layer is from about 30 Å to about 100 Å. Another illustrative range is  
23 from about 50 Å to about 500 Å. Of course, a thickness outside of this range can also  
24 be used.

25 Where the charge injecting layer and the light absorbing layer may undesirably  
26 react with one another if the two layers are in contact, or where the charge injecting  
27 layer may be damaged during coating of the light absorbing layer on it, thereby  
28 degrading the performance of the organic light emitting device, the presence of an  
29 intervening buffer layer will prevent or minimize such reactions or damage. A buffer  
30 layer, therefore, will include a material that may not undesirably react with both the  
31 charge injecting layer and the light absorbing layer, and also that may protect the charge  
32 injecting layer from possible damage during coating of the light absorbing layer on it.  
33 Examples of materials that can be selected to comprise the buffer layer are metallic  
34 compounds such as metal oxides like  $\text{Al}_2\text{O}_3$ , metal halides like  $\text{MgF}_2$ , and others.  
35 Other materials that can be selected to form the buffer layer include porphyrins like

1 metal phthalocyanine such as copper phthalocyanine. Preferred materials that can be  
2 used include SiO, SiO<sub>2</sub> or mixtures thereof. The buffer layer is preferably non-  
3 reflective. In embodiments, the buffer layer is partially or substantially transparent  
4 and/or light absorbing.

5 The thickness of the buffer layer is selected depending on the materials used to  
6 form this buffer layer such that significant cross directional conduction from the  
7 electrically conductive light absorbing layer to the charge injecting layer across the  
8 buffer layer is not interrupted by the buffer layer. Typically, the thickness of the buffer  
9 layer can range from about 10 Å to about 5,000 Å, particularly from about 50 Å to  
10 about 1,000 Å.

11 The electrically conductive light absorbing layer can include a single material  
12 that combines the desired light absorption and electrical conduction properties such as  
13 carbon (e.g., graphite and C<sub>60</sub>), Si, Ge and the like, a metal such as Mo, Ni, Cr, Pd, V,  
14 Se, In and their alloys such as INCONEL™, NICHROME™, and the like, or a  
15 conductive light absorbing metal oxide. The electrically conductive light absorbing  
16 layer can also be comprised of a blend of two or more materials, wherein at least one of  
17 the materials is a light absorbing material such as an organic dye or pigment, such as a  
18 phthalocyanine, a perinone, a perylene, a perylene dimer, and the like, and wherein one  
19 of the materials is a conductive material, such as a metal like Ag, Al, Au, Cu, Mg, In  
20 and the like. When the light absorbing layer is comprised of two or more materials, the  
21 concentration of each material in the layer can be adjusted in order to obtain the desired  
22 electrical conduction and light absorption properties. For example, the layer can  
23 comprise from about 50 volume percent to about 99 volume percent of a light  
24 absorbing material and from about 50 volume percent to about 1 volume percent of an  
25 electrically conductive material.

26 The electrically conductive light absorbing layer may have a thickness ranging  
27 for example from about 10 Å to about 10,000 Å, where preferred ranges for the  
28 thickness can be selected depending on the materials used in forming the layer. One  
29 illustrative thickness range is from about 10 Å to about 500 Å. Another illustrative  
30 thickness range is from about 500 Å to about 5,000 Å. Yet, another illustrative  
31 thickness range is from about 5,000 Å to about 10,000 Å. Of course, a thickness  
32 outside of these ranges can also be used.

33 The phrase "light absorbing" indicates noticeable extinction of light, for example,  
34 at least about 50% extinction of light entering the light absorbing layer, particularly at  
35 least about 90% extinction of light entering the light absorbing layer. The light

1 absorbing layer functions on a different principle from that of an optical interference  
2 layer. The light absorbing layer relies on light absorption, whereas the optical  
3 interference layer relies on destructive light interference. Thus, the light absorbing  
4 layer achieves a noticeable extinction of light without relying on destructive light  
5 interference.

6 In embodiments, the ohmic resistance for cross directional conduction across the  
7 light absorbing layer does not exceed an illustrative value of about 100 ohms; in  
8 particular, the ohmic resistance does not exceed another illustrative value of about 10  
9 ohms; in embodiments, the ohmic resistance does not exceed still another illustrative  
10 value of about 1 ohm.

11 Where the collective sheet resistance of the charge injecting layer and the  
12 electrically conductive light absorbing layer is too high to sustain significant lateral  
13 conduction, such as if the collective sheet resistance of the charge injecting layer and  
14 the electrically conductive light absorbing layer exceeds an illustrative value of about 5  
15 ohms per square, or if the light absorbing layer (or any layers underneath it) is degraded  
16 as a result of exposure to external environment thereby degrading the performance of  
17 the organic light emitting device, a protective metallic layer coated on the light  
18 absorbing layer can be used to lower the sheet resistance of the electrode containing the  
19 light absorbing layer or to prevent (or at least reduce) the damage caused to the device  
20 by the external environment.

21 The optional metallic layer can be composed of any suitable metal such as Ag,  
22 Au, Al, Mg, In, Ca, Sr and the like, or alloys thereof such as Mg:Ag alloys composed  
23 of, for example, from about 80 to 95 volume percent of Mg and about 20 to about 5  
24 volume percent of Ag, and Li:Al alloys, composed of, for example, from about 90 to 99  
25 volume percent of Al, and from about 10 to about 1 volume percent of Li.

26 The optional metallic layer preferably is thick enough in order to achieve a  
27 reduced sheet resistance such as less than about 5 ohms per square, and particularly  
28 even less than about 1 ohm per square, and also preferably is thick enough to  
29 effectively isolate the light absorbing layer from external environment. However, there  
30 is no particular upper limit for the thickness except as may be required by device  
31 fabrication considerations. Typically, the metallic layer may have a thickness ranging  
32 for example from about 100 Å to about 10,000 Å, and more particularly from about  
33 1,000 Å to about 4,000 Å. Of course, a thickness outside of these ranges can also be  
34 used.

1           The luminescent region is composed of an organic electroluminescent material.  
2       Electroluminescent materials include, for example, polyphenylenevinylenes such as  
3       poly(p-phenylenevinylene) PPV, poly(2-methoxy-5-(2-ethylhexyloxy)1,4-  
4       phenylenevinylene) MEHPPV and poly(2,5-dialkoxyphenylenevinylene) PDMeOPV,  
5       and other materials disclosed in U.S Patent 5,247,190, which is incorporated herein by  
6       reference in its entirety; polyphenylenes, such as poly(p-phenylene) PPP, ladder-poly-  
7       para-phenylene (LPPP), and poly(tetrahydropyrene) PTHP; and polyfluorenes, such as  
8       poly(9,9-di-n-octylfluorene-2,7-diyl), poly(2,8-(6,7,12,12-tetraalkylindenofluorene)  
9       and copolymers containing fluorenes such as fluorene-amine copolymers (see e.g.,  
10      Bernius et al., "Developmental Progress of Electroluminescent Polymeric Materials  
11      and Devices," Proceedings of SPIE Conference on Organic Light Emitting Materials  
12      and Devices III, Denver, Colorado, July 1999, Volume 3797, p. 129).

13           Another class of organic electroluminescent materials that can be utilized in the  
14      luminescent region includes, but is not limited to, the metal oxinoid compounds as  
15      disclosed in U.S. Patents 4,539,507; 5,151,629; 5,150,006; 5,141,671 and 5,846,666,  
16      each incorporated herein by reference in its entirety. Illustrative examples include  
17      tris(8-hydroxyquinolate) aluminum (AlQ3), which is one preferred example, and  
18      bis(8-hydroxyquinolato)-(4-phenylphenolato) aluminum (BALq) which is another  
19      preferred example. Other examples of this class of materials include tris(8-  
20      hydroxyquinolate) gallium, bis(8-hydroxyquinolate) magnesium, bis(8-  
21      hydroxyquinolate) zinc, tris(5-methyl-8-hydroxyquinolate) aluminum, tris(7-  
22      propyl-8-quinolinolato) aluminum, bis[benzo{f}-8-quinolate]zinc, bis(10-  
23      hydroxybenzo[h]quinolate) beryllium, and the like, and metal thioxinoid compounds  
24      disclosed in U.S. Patent 5,846,666 (which is incorporated herein by reference in its  
25      entirety), such as metal thioxinoid compounds of bis(8-quinolinethiolato)zinc, bis(8-  
26      quinolinethiolato)cadmium, tris(8-quinolinethiolato)gallium, tris(8-  
27      quinolinethiolato)indium, bis(5-methylquinolinethiolato)zinc, tris(5-  
28      methylquinolinethiolato)gallium, tris(5-methylquinolinethiolato)indium, bis(5-  
29      methylquinolinethiolato)cadmium, bis(3-methylquinolinethiolato)cadmium, bis(5-  
30      methylquinolinethiolato)zinc, bis[benzo{f}-8-quinolinethiolato]zinc, bis[3-  
31      methylbenzo{f}-8-quinolinethiolato]zinc, bis[3,7-dimethylbenzo{f}-8-  
32      quinolinethiolato]zinc, and the like. Preferred materials are bis(8-  
33      quinolinethiolato)zinc, bis(8-quinolinethiolato)cadmium, tris(8-  
34      quinolinethiolato)gallium, tris(8-quinolinethiolato)indium and bis[benzo{f}-8-  
35      quinolinethiolato]zinc.

1 More specifically, a class of organic electroluminescent materials that can be  
2 used in the luminescent region comprises stilbene derivatives, such as those disclosed  
3 in U.S. Patent 5,516,577, incorporated herein by reference in its entirety. A preferred  
4 stilbene derivative is 4,4'-bis(2,2-diphenylvinyl)biphenyl.

5 Another class of suitable organic electroluminescent materials suitable for  
6 utilizing in the luminescent region is the oxadiazole metal chelates. These materials  
7 include bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]zinc; bis[2-(2-  
8 hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(1-  
9 naphthyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-  
10 oxadiazolato]beryllium; bis[5-biphenyl-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]zinc;  
11 bis[5-biphenyl-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]beryllium; bis(2-  
12 hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]lithium; bis[2-(2-hydroxyphenyl)-5-p-  
13 tolyl-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-p-tolyl-1,3,4-  
14 oxadiazolato]beryllium; bis[5-(p-tert-butylphenyl)-2-(2-hydroxyphenyl)-1,3,4-  
15 oxadiazolato]zinc; bis[5-(p-tert-butylphenyl)-2-(2-hydroxyphenyl)-1,3,4-  
16 oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(3-fluorophenyl)-1,3,4-  
17 oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-fluorophenyl)-1,3,4-  
18 oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-fluorophenyl)-1,3,4-  
19 oxadiazolato]beryllium; bis[5-(4-chlorophenyl)-2-(2-hydroxyphenyl)-1,3,4-  
20 oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-methoxyphenyl)-1,3,4-  
21 oxadiazolato]zinc; bis[2-(2-hydroxy-4-methylphenyl)-5-phenyl-1,3,4-  
22 oxadiazolato]zinc; bis[2- $\alpha$ -(2-hydroxynaphthyl)-5-phenyl-1,3,4-oxadiazolato]zinc;  
23 bis[2-(2-hydroxyphenyl)-5-p-pyridyl-1,3,4-oxadiazolato]zinc; bis[2-(2-  
24 hydroxyphenyl)-5-p-pyridyl-1,3,4-oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-  
25 (2-thiophenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-  
26 thiadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-thiadiazolato]beryllium;  
27 bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-thiadiazolato]zinc; and bis[2-(2-  
28 hydroxyphenyl)-5-(1-naphthyl)-1,3,4-thiadiazolato]beryllium, and the like; and the  
29 triazines including those disclosed in U.S. Patent 6,057,048, which is incorporated  
30 herein by reference in its entirety.

31 The luminescent region can further include from about 0.01 weight percent to  
32 about 25 weight percent of a luminescent material as a dopant. Examples of dopant  
33 materials that can be utilized in the luminescent region are fluorescent materials, such  
34 as coumarin, dicyanomethylene pyranes, polymethine, oxabenzanthrane, xanthene,  
35 pyrylium, carbostyl, perylene, and the like. Another preferred class of fluorescent

1 materials are quinacridone dyes. Illustrative examples of quinacridone dyes include  
2 quinacridone, 2-methylquinacridone, 2,9-dimethylquinacridone, 2-chloroquinacridone,  
3 2-fluoroquinacridone, 1,2-benzoquinacridone, N,N'-dimethylquinacridone, N,N'-  
4 dimethyl-2-methylquinacridone, N,N'-dimethyl-2,9-dimethylquinacridone, N,N'-  
5 dimethyl-2-chloroquinacridone, N,N'-dimethyl-2-fluoroquinacridone, N,N'-dimethyl-  
6 1,2-benzoquinacridone, and the like as disclosed in U.S. Patents 5,227,252; 5,276,381  
7 and 5,593,788, each incorporated herein by reference in its entirety. Another class of  
8 fluorescent materials that may be used is fused ring fluorescent dyes. Exemplary  
9 suitable fused ring fluorescent dyes include perylene, rubrene, anthracene, coronene,  
10 phenanthrene, pyrene and the like, as disclosed in U.S. Patent 3,172,862, which is  
11 incorporated herein by reference in its entirety. Also, fluorescent materials include  
12 butadienes, such as 1,4-diphenylbutadiene and tetraphenylbutadiene, and stilbenes, and  
13 the like, as disclosed in U.S. Patents 4,356,429 and 5,516,577, each incorporated herein  
14 by reference in its entirety. Other examples of fluorescent materials that can be used  
15 are those disclosed in U.S. Patent 5,601,903, which is incorporated herein by reference  
16 in its entirety.

17 Additionally, luminescent dopants that can be utilized in the luminescent region  
18 are the fluorescent dyes disclosed in U.S. Patent 5,935,720 (which is incorporated  
19 herein by reference in its entirety) such as 4-(dicyanomethylene)-2-*I-propyl*-6-(1,1,7,7-  
20 tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTb); the lanthanide metal chelate  
21 complexes, such as for example, tris(acetylacetonato)(phenanthroline) terbium,  
22 tris(acetylacetonato)(phenanthroline) europium, and tris(thenoyl  
23 trisfluoroacetato)(phenanthroline) europium, and those disclosed in Kido et al.,  
24 "White light emitting organic electroluminescent device using lanthanide complexes,"  
25 Jpn. J. Appl. Phys., Volume 35, pp. L394-L396 (1996), which is incorporated herein by  
26 reference in its entirety; and phosphorescent materials, such as organometallic  
27 compounds containing heavy metal atoms that lead to strong spin-orbit coupling, such  
28 as those disclosed in Baldo et.al., "Highly efficient organic phosphorescent emission  
29 from organic electroluminescent devices," Letters to Nature, Volume 395, pp. 151-154  
30 (1998), which is incorporated herein by reference in its entirety. Preferred examples  
31 include 2,3,7,8,12,13,17,18-octaethyl-21*H*23*H*-phorpine platinum(II) (PtOEP) and *fac*  
32 tris(2-phenylpyridine)iridium (Ir(ppy)<sub>3</sub>).

33 The luminescent region can also include one or more materials with hole-  
34 transporting properties. Examples of hole-transporting materials that can be utilized in  
35 the luminescent region include polypyrrole, polyaniline, poly(phenylene vinylene),

polythiophene, polyarylamine as disclosed in U.S. Patent 5,728,801, which is incorporated herein by reference in its entirety, and their derivatives, and known semiconductive organic materials; porphyrin derivatives such as 1,10,15,20-tetraphenyl-21H,23H-porphyrin copper (II) disclosed in U.S. Patent 4,356,429, incorporated herein by reference in its entirety; copper phthalocyanine, copper tetramethyl phthalocyanine; zinc phthalocyanine; titanium oxide phthalocyanine; magnesium phthalocyanine; and the like

A specific class of hole transporting materials that can be utilized in the luminescent region are the aromatic tertiary amines such as those disclosed in U.S. Patent 4,539,507, which is incorporated herein by reference in its entirety. Suitable exemplary aromatic tertiary amines include, but are not limited to, bis(4-dimethylamino-2-methylphenyl)phenylmethane, N,N,N-tri(p-tolyl)amine, 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane, 1,1-bis(4-di-p-tolylaminophenyl)-4-phenyl cyclohexane, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-bis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine, N,N,N',N'-tetra-p-tolyl-1,1'-biphenyl-4,4'-diamine, N,N'-di-1-naphthyl-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine, mixtures thereof and the like. Another class of aromatic tertiary amines are polynuclear aromatic amines. Examples of these polynuclear aromatic amines include, but are not limited to, N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]aniline; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]aniline; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-p-chlorophenylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-chlorophenylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-chlorophenylamino)-4-biphenyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-p-chloroaniline; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]-m-chloroaniline; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-1-aminonaphthalene, mixtures thereof and the like; 4,4'-bis(9-carbazolyl)-1,1'-biphenyl compounds, such as 4,4'-bis(9-carbazolyl)-1,1'-biphenyl and 4,4'-bis(3-methyl-9-carbazolyl)-1,1'-biphenyl, and the like.

A specific class of the hole transporting materials that can be used in the luminescent region are the indolo-carabazoles, such as those disclosed in U.S. Patents 5,942,340 and 5,952,115, each incorporated herein by reference in its entirety, such as

1 5,11-di-naphthyl-5,11-dihydroindolo[3,2-b]carbazole, and 2,8-dimethyl-5,11-di-  
2 naphthyl-5,11-dihydroindolo[3,2-b]carbazole; N,N,N',N'-tetraarylbenzidines, wherein  
3 aryl may be selected from phenyl, m-tolyl, p-tolyl, m-methoxyphenyl, p-  
4 methoxyphenyl, 1-naphthyl, 2-naphthyl and the like. Illustrative examples of  
5 N,N,N',N'-tetraarylbenzidine are N,N'-di-1-naphthyl -N,N'- diphenyl-1,1'-biphenyl-4,4'-  
6 diamine, which is more preferred; N,N'-bis(3-methylphenyl) -N,N'- diphenyl-1,1'-  
7 biphenyl-4,4'-diamine; N,N'-bis(3-methoxyphenyl) -N,N'- diphenyl-1,1'-biphenyl-4,4'-  
8 diamine, and the like. Preferred hole transporting materials that can be used in the  
9 luminescent region are the naphthyl-substituted benzidine derivatives.

10 The luminescent region can also include one or more materials with electron  
11 transporting properties. An example of electron transporting materials that can be  
12 utilized in the luminescent region is polyfluorenes, such as poly(9,9-di-n-octylfluorene-  
13 2,7-diyl), poly(2,8-(6,7,12,12-tetraalkylindenofluorene) and copolymers containing  
14 fluorenes such as fluorene-amine copolymers, as disclosed in incorporated Bernius et  
15 al., Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices  
16 III, Denver, Colorado, July 1999, Volume 3797, p. 129.

17 Other examples of electron transporting materials that can be utilized in the  
18 luminescent region can be selected from the metal oxinoid compounds, the oxadiazole  
19 metal chelate compounds, the triazine compounds and the stilbene compounds,  
20 examples of which have been described above in detail.

21 In embodiments where the luminescent region includes one or more hole  
22 transport material and/or one or more electron transport material in addition to the  
23 organic electroluminescent material(s), the organic electroluminescent material, the  
24 hole transport material(s), and/or the electron transport material(s) can be formed in  
25 separate regions, such as the OLEDs disclosed in U.S. Patents 4,539,507; 4,720,432  
26 and 4,769,292; or in the same region thus forming mixed regions of two or more  
27 materials, such as the OLEDs disclosed in U.S. Patent 6,130,001, and in U.S.  
28 Application Serial Nos. 09/357,551, filed on July 20, 1999; 09/606,670, filed on June  
29 30, 2000; and 09/770,159, filed on January 26, 2001. The disclosures of these patents  
30 and patent applications are incorporated herein by reference in their entirety.

31 The thickness of the luminescent region can vary for example, from about 10 Å  
32 to about 10,000 Å, typically from about 200 Å to about 2,000 Å, and particularly from  
33 about 500 Å to about 1,500 Å. In embodiments wherein the luminescent region  
34 includes two or more layers, the thickness of each layer can, for example, be from



1 about 10 Å to about 5,000 Å, typically from about 50 Å to about 2,000 Å, and  
2 particularly from about 100 Å to about 1,500 Å.

3 The organic light emitting device can be fabricated by sequentially forming the  
4 layers comprising the organic light emitting device on the substrate, using any suitable  
5 thin film forming technique, typically, spin coating or deposition by thermal  
6 evaporation in vacuum. In embodiments, the charge injecting layer, the light  
7 absorbing layer, and the optional buffer layer and metallic layer are deposited by  
8 thermal evaporation in vacuum.

9 More details about fabrication and operation of organic light emitting devices are  
10 disclosed, for example, in U.S. Patents 4,539,507 and 4,769,292, and in copending  
11 U.S. Applications No. 09/357,551, filed on July 20, 1999; No. 09/606,670, filed on  
12 June 30, 2000; and No. 09/770,159, filed on January 26, 2001, the disclosure of each  
13 patent and patent application being totally incorporated herein by reference.

14 The invention will now be described in detail with respect to specific preferred  
15 embodiments thereof, it being understood that these examples are intended to be  
16 illustrative only and the invention is not intended to be limited to the materials,  
17 conditions, or process parameters recited herein. All percentages and parts are by  
18 weight unless otherwise indicated.

## 20 EXAMPLE

21  
22 An inventive organic light emitting device according to the device structure of  
23 FIG. 1 was fabricated. The organic light emitting device was composed of in the  
24 sequence:

- 25 a substrate made of glass of about 1 mm thickness;
- 26 an anode composed of indium tin oxide of about 200 nm thickness;
- 27 a luminescent region composed of a hole transport layer of thickness about 60 nm  
28 coated on the anode, made of *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine  
29 (NPB), and a luminescent electron transport layer, about 75 nm thick, coated on the  
30 hole transport layer made of tris (8-hydroxyquinoline) aluminum (AlQ3); and
- 31 a cathode including: (a) a substantially transparent electron injecting layer, about  
32 4 nm thick, made of Mg:Ag alloy (9:1 by volume), (b) a buffer layer, about 200 nm  
33 thick, made of SiO, (c) a light absorbing layer, about 500 nm thick, made of a black  
34 pigment material, Bis (1,8-Naphthimidazo) perinone, and (d) a metallic layer, about  
35 200 nm thick, made of Ag.

## COMPARATIVE EXAMPLE

A comparative organic light emitting device, similar to the inventive OLED of the Example but which included a conventional cathode, was fabricated and evaluated. The organic light emitting device was composed of in the sequence:

a substrate made of glass of thickness about 1 mm;

an anode composed of indium tin oxide, of thickness about 200 nm;

a luminescent region, composed of a hole transport layer of thickness about 60 nm coated on the anode, made of *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB), and a luminescent electron transport layer, about 75 nm thick, coated on the hole transport layer made of tris (8-hydroxyquinoline) aluminum (AlQ3); and

a cathode including: (a) an electron injecting layer, about 120 nm thick, made of Mg:Ag alloy (9:1 by volume); and (b) a metallic layer, about 80 nm thick, made of Ag.

Both the inventive and comparative organic light emitting devices including the cathode layers were fabricated by thermal evaporation in vacuum (about  $5 \times 10^{-6}$  torr.) in the same pump down cycle.

Visual examination of the inventive and comparative organic light emitting devices revealed negligible reflectivity of the cathode of the inventive organic light emitting device, whereas the cathode of the comparative organic light emitting device was highly reflective of ambient illumination, giving it a mirror-like appearance.

When operated under 7 volts, emission from the inventive organic light emitting device demonstrated excellent visibility, regardless of the viewing angle, even when viewed under strong ambient illumination from a 200W flood light source placed about 15 cms apart from the device. On the other hand, emission from the comparative organic light emitting device, when operated under 7 volts, was almost invisible under the same ambient illumination conditions.

Other modifications of the present invention may occur to those skilled in the art based upon a reading of the present disclosure and these modifications are intended to be included within the scope of the present invention.